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RESEARCH ARTICLE

STUDIES OF STRUCTURAL AND OPTICAL PROPERTIES OF ZNO NANORODS AND ITS INFLUENCE OF pH

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ABSTRACT

Zinc Oxide (ZnO) nano rods arrays have been grown on glass substrates with different pH by using a seed layer. ZnO seed layer thin films were prepared by Chemical Bath Deposition (CBD) method on glass substrates. Ammonia was used to achieve the desired pH value. ZnO seed coated thin films were immersed in aqueous solution for 4 hours at 90°C. Zinc nitrate hexahydrate was used as source of zinc ion, while hexamethylenetetramine solution served as the complexing agent. The effect of pH of precursor solution on the structural and optical properties of ZnO nano rods was investigated. They were characterized by means of XRD, SEM, UV-Vis spectroscopy and PL. XRD results indicated that the prepared nano rods were hexagonal wurzite structure. The optical measurement shows that there is a change in the band gap of nano rod arrays with changing the pH of the starting solution. SEM images reveal that the change in the pH value from 6.5 to 9 leads to change in the size of nano rods grown on substrate.

INTRODUCTION

Thin films of Zinc Oxide (ZnO) have attracted great attention for their applications in semiconductor devices, acoustic wave and acoustic – optical devices, photoconductors, piezoelectric properties, high transparency in the visible range and high light trapping characteristics [1]. Zinc Oxide is an n-type semiconductor with a direct bandgap of 3.37eV at room temperature and excitation binding energy of 60 meV. Most prominent crystalline structure of ZnO is wurtzite type, although, it also exists in the cubic Zincblende and rocksalt structures [2-3]. The optical and structural properties of ZnO depend on physical and chemical parameters such as preparative methods, drying process, annealing temperature, pH of solution, chemical composition and growth conditions. Much effort has been devoted to the development of ZnO nano structures by different methods such as sputtering, Molecular Beam Epitaxy (MBE), thermal evaporation, chemical vapour deposition (CVD), Spray pyrolysis, aqueous chemical and hydrothermal methods. Among these methods, the hydrothermal method is promising for fabricating ideal nanomaterial with special morphology because of the simple, fast, less expensive, low growth temperature, high yield and scaleable [4]. In this work, we compare the optical and structural properties of the ZnO nano rods are prepared by different pH. The effect of pH on the optical and structural properties of ZnO nano rods is reported.

Experimental

ZnO thin films were prepared by using the sol – gel method and deposited onto glass substrates by the dip coating technique. Three different pH were used for the deposition of ZnO thin films. 0.1 mole Zinc acetate was dissolved into 10 ml of ethanol. Then the 0.25 ml of distilled water was introduced drop by drop. Under stirring the solution was transferred into a clear homogeneous solution. The above solution was used as seed layer and deposited on glass substrates which are cleaned by detergent and then completely rinsed in acetone and deionised water respectively, and dried in air. pH of as-prepared starting solution was measured as 6.5. The solution was taken in a beaker and the glass substrates were dipped into 5 times at regular intervals at room temperature by Chemical Bath Deposition method. Then the 5 layer films were annealed in a furnace at the temperature of 200°C for 1 hour. The pH of starting solution was adjusted to desired value using ammonia (NH_4OH). The starting solution was prepared by adjusting pH 6.5, 7.5 and 9. The ZnO nano rods were grown by hydrothermal method from 0.02 mole of Zinc nitrate ($(Zn(NO)_3)_2.6H_2O$) and 0.2 mole of hexamethylenetetramine (HMT,$C_6H_{12}N_4$) on 1:10 molar concentration. The resultant solution was stirred at room temperature for 2 hours. Hydrothermal growth was carried out at 90°C in a sealed beaker placed on a hotplate for 4 hours. The prepared films were washed with distilled water and then finally dried at room temperature in air. Then the above films onto glass substrate were annealed at 500°C for 1 hour in order to obtain the ZnO nano rods. The crystal structure of ZnO nano rods arrays were investigated by X-ray diffractometer(XRD) with Cu Kα radiation. The surface morphologies were observed using Scanning Electron Microscope (SEM) and the transmittance and absorbance of the films in the visible region was measured using JASUO corp. V-570 spectrometer.

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RESULTS AND DISCUSSION

Structure and Morphology

The pH of the precursor solution was found to play a major role in the deposition of ZnO nanorod arrays. For pH value 6.5 and 7.5 only poor quantity deposition are produced. For pH 9 no deposition was obtained. The reason for this should be higher reaction rate, when precipitates start to dissolve. ZnO nano rods have been prepared by the multi coating method using three different pH values of 6.5, 7.5 and 9. The entire films have been annealed at 500°C. Figure 1 shows the X-ray pattern of pH 6.5 ZnO films. The patterns of the ZnO naorods array films deposited on glass revealed three dominant peaks at 2θ 32.2°, 34.7° and 36.4° corresponding to (100), (002) and (101) planes respectively. The strongest reflection observed along the (002) direction for all samples indicates that the ZnO nanorods arrays are preferentially well-oriented in the direction of the c-axis. From figure 1 the intensities of the reflection peaks change as the pH increases from 6.5 to 7.5. In the presence of small peaks in pH 6.5 the (h.k,l) peaks were detected at 32.2°, 34.7°, 36.4° corresponding to the lattice planes (100), (002) and (101) respectively. The XRD pattern of pH 6.5 shows that, it has a strong (002) peak and weak (100) and (101) peaks. The pH value increases from 6.5 to 7.5, the intensity of the (100), (002) and (101) peaks has been increased. The presence of broad peaks in the pH 7.5 samples shows that the grains have started to grow on pH and the films are of nano crystalline nature.

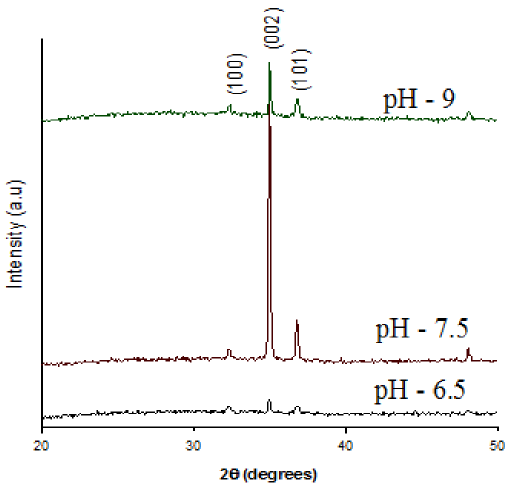


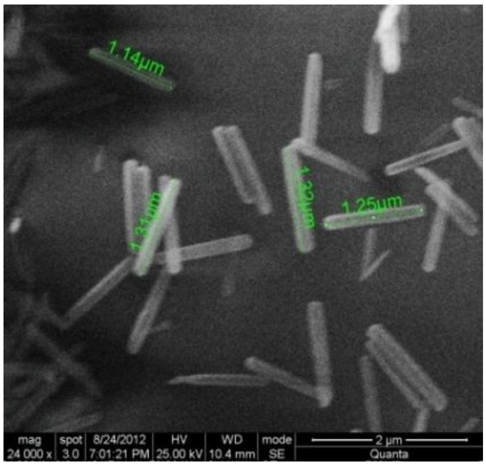
Figure 1. The X-ray Diffraction pattern of ZnO nano rods prepared at three different pH values.

The pH value increases from 7.5 to 9, the intensity of the (100), (002) and (101) peaks has been decreased. The diffraction pattern of pH 9 ZnO films shows small reflection peaks, which indicates the formation of small crystallites. The strong and narrow diffraction peaks indicate that the material has a good crystalline and size [5-7]. The full width at half maximum (FWHM) of ZnO thin films for (002) plane are given in Table 1. FWHM of ZnO thin films shows as change with changing pH values. The grain size d of crystallites was calculated using Debey Scherrer's formula.

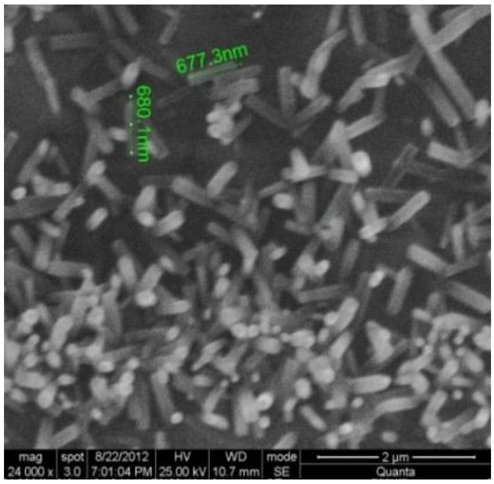
Table 1. The structural parameters of ZnO thin films

Samples	FWHM	2θ (angle)	Grain size d (nm)
pH 6.5	0.30	34.97	27.7
pH 7.5	0.21	35.03	39.6
pH 9	0.26	35.08	32.05

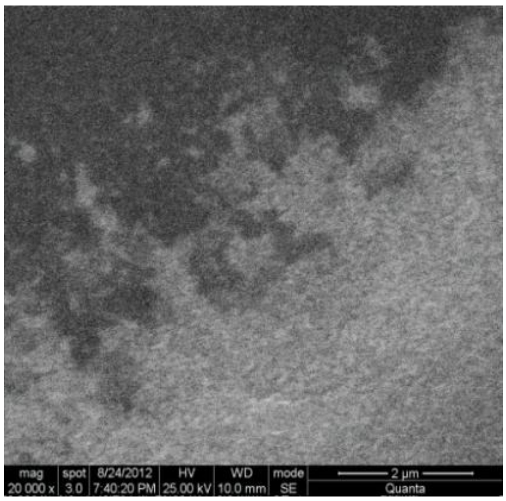
The SEM micrographs recorded at 25 kV with magnification 24 K. SEM images of ZnO nanorods arrays grown with different pH value ranging from 6.5, 7.5 and 9 are shown in figure 2. As can be seen from SEM images, the orientation of the obtained ZnO rod arrays strongly depends on the pH of the starting solution. Although seed layers are on the substrates, it can be seen clearly that the samples produced from solution with pH 6.5 and pH 7.5 consist of well-aligned nanorods with diameter 150-200nm and most of the nanorods are straight. The lengths of the nanorods are from 1 to 2 microns. The ZnO rod arrays obtained from solution with 9 pH were randomly oriented al low density on the entire substrate. From SEM observations, it is clear that the morphological characteristics of annealed 500°C ZnO structure can be markedly controlled by the pH value of starting solution with using seed layer. In addition, as clearly seen from SEM images, although the shape of the structures remains the same their overall dimensions change with increasing pH. In other words, one can tune-up the size of the ZnO structures from macro to nanorods by adjusting the pH of the solution [8-10].



(a) pH 6.5 of ZnO Film



(a) pH 6.5 of ZnO Film



(c) pH 9 of ZnO Film

Figure 2. SEM pictures of ZnO nanorods deposited on glass substrates with pre-deposited ZnO seed for different pH values

Optical characterization (UV-Vis Spectroscopy)

The absorbance spectrum of ZnO nanorods synthesized at various pH conditions were examined by UV-Vis spectroscopy. Figure 3 shows the UV-Vis absorption spectra of ZnO nano rods prepared at three different pH 6.5, 7.5 and 9 respectively.

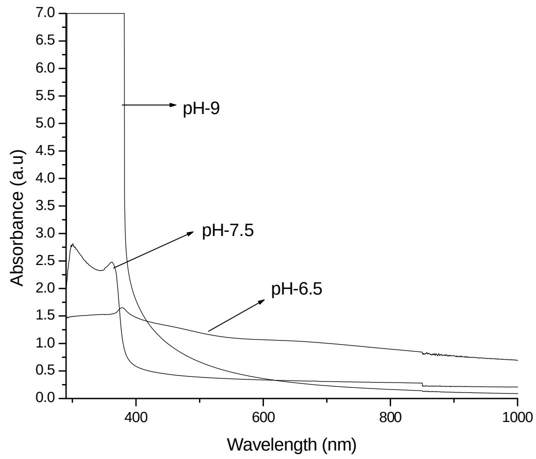


Figure 3. UV Vis Absorption spectrum of ZnO thin film

The optical absorption edge has a trend to shift to a higher wavelength with changing their pH value. Broad peaks have been found in the pH value of 6.5 and 7.5 in the range of 350nm – 400nm. Which is a characteristic / standard peak of wurtzite hexagonal phase ZnO. Demonstrating that the synthesized products are pure ZnO and due to the presence of a broad peak in the obtained UV-Vis spectra, one can easily conclude that the grown ZnO nano structures exhibited good optical properties and containing wurtzite hexagonal phase. The optical absorption determines the optical band gap and ZnO films have a direct band gap. The optical band gap of ZnO films was found to decrease from 3.45 eV to 3.22 eV, 3.16 eV and 3.09 eV with the increase of pH. The decrease in band gap of ZnO films may be attributed to the improvement in the crystalline quality of the films along with reduction in porosity and increase of grain size. Optical transmittance spectra of ZnO films prepared at different pH values6.5, 7.5 & 9. Figure 4 shows the UV-Vis absorption spectra of ZnO nano rods prepared at three different pH 6.5, 7.5 and 9 respectively.

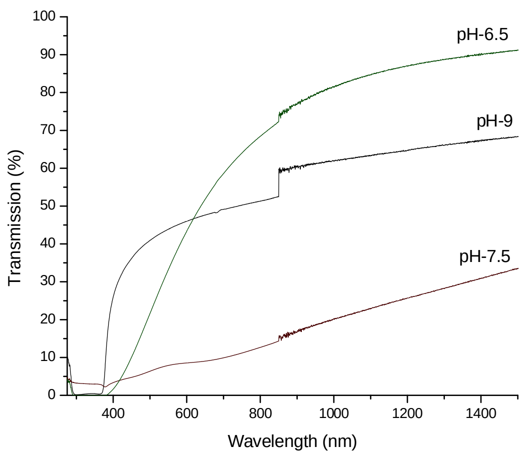


Figure 4. UV Vis Transmission spectrums of ZnO thin films

The transmittance for the film prepared at pH 6.5 was observed to be the highest. ie, ~90% at 850 nm. pH 7.5 was observed to be the ~30% at 850 nm and the pH 9 was observed to be the ~70% at 850 nm. The transmittance of the film is observed to decrease with increase in pH value. This can be described to the formation of large particles on the surface of ZnO thin films with increase of pH value which causes scattering of light. The optical transmittance of ZnO films was found to decrease from 90%, 70% to 30% with changing pH value [11-15].

PL Characteristics

The ZnO nanostructures grown by hydrothermal growth are of nanorod shape, vertically orientated and fairly uniformly distributed over the substrate surface. The nanostructures are hexagonally faceted, reflecting the ZnO crystal structure and have characteristic dimensions of 150 - 200 nm in diameter and 1-2 µm in length. Photoluminescence (PL) is a powerful tool for probing the light emission properties of semiconductors. Particularly, temperature dependent PL studies can give comprehensive information about the nature of the light emission and reveal the fundamental material properties. Figure 5 shows the PL spectra of ZnO nano rods prepared at three different pH 6.5, 7.5 and 9 respectively.

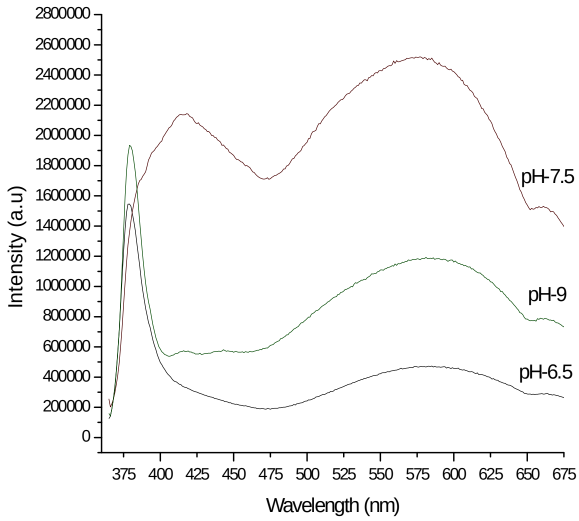


Figure 5. PL spectra of ZnO nanorods deposited at three different pH

The spectra were recorded with excitation wavelength of 350 nm for detecting PL peaks in the range of 350 – 675 nm. PL spectra of ZnO nanorods deposited at three different pH PL spectra for the ZnO nanorods having different aspect ratios are shown in figure 5, which are dominated by the pH 6.5 presence of a strong PL peaks at 378nm (3.28eV) followed by a low intensity peak at 586nm (2.12eV). The pH 7.5 presence of a strong peaks at 381nm (3.26eV) followed by a low intensity peak at 582nm (2.13eV) and the pH 9 presence of a strong peaks at 420nm (2.95eV) followed by a low intensity peak at 577nm (2.15eV). It is known that undoped ZnO, having large excitation binding energy is known to exhibit PL emission peaks due to donor bound excitation and free excitation. The peak at ~ 570nm and ~581nm may arise due to transitions from deep donor states arising out of oxygen vacancy located below the conduction band to the valance band. The overall emission of this structure is high, providing strong visible luminescence in the range 350 – 675 nm [16-19].

Conclusion

The Zinc Oxide arrays were grown on the glass substrates with changing their pH 6.5, pH 7.5 and pH 9 by using a simple hydrothermal method with using seed layer. The size of the ZnO rod arrays was found to depend on pH value of precursor solution. The ZnO films are characterized by means of XRD, SEM, UV and PL and the conclusion was drawn. The XRD analysis reveals that the structures of the all ZnO films are expected to be a hexagonal wurzite structure. The grain size of crystallites was found to be in the range of 27nm to 32nm. All the samples indicated enhanced intensities for the peaks corresponding to (002) plane indicating preferential orientation along the c-axis. From the SEM observation it was concluded that the ZnO rod arrays can be grown from microrod size to nanorod size by adjusting pH of precursor solution. Therefore, one can control the size of the ZnO crystal structures by adjusting the pH of the solution. In the presence of a broad peak in the obtained UV-Vis spectra, one can easily conclude that the grown ZnO nano structures exhibited good optical properties and containing wurtzite hexagonal phase. The optical band gaps in ZnO films by various pH values are from 3.45eV to 3.09eV. The present experiments show that the different pH values would influence morphological and optical properties of the prepared ZnO nanorods.

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